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13. ABSTRACT (Maximum 200 Words) This project consists of experiments and theoretical modeling designed to improve our understanding of the detailed chemical kinetics of supercritical water oxidation processes. The objective of the four-year project is to develop working models that accurately predict the oxidation rates and mechanisms for a variety of key organic species over the range of temperatures and pressures important for industrial applications. Our examination of reaction kinetics in supercritical water undertakes in situ measurements of reactants, intermediates, and products using optical spectroscopic techniques, primarily Raman spectroscopy. Our focus is to measure the primary oxidation steps that occur in the oxidation of methanol, higher alcohols, methylene chloride, aromatics, and some simple organic compounds containing nitro groups. We are placing special emphasis on identifying reaction steps that involve hydroxyl radicals, hydroperoxyl radicals, and hydrogen peroxide. The measurements are conducted in two optically accessible reactors located at Sandia's Combustion Research Facility (CRF), the supercritical flow reactor (SFR) and the supercritical constant volume reactor, designed to operate at temperatures and pressures up to 600 °C and 500 MPa. The combination of these two reactors permits reaction rate measurements ranging from 0.1 s to many hours.				
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Kinetics of Supercritical Water Oxidation

SERDP Compliance Technical Thrust Area

Quarterly Report

Sandia National Laboratories
Combustion Research Facility
Case 8610.000

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Reporting Period: April 1 - June 30, 1996

Project description

This project consists of experiments and theoretical modeling designed to improve our understanding of the detailed chemical kinetics of supercritical water oxidation (SCWO) processes. The objective of the five-year project is to develop working models that accurately predict the oxidation rates and mechanisms for a variety of key organic species over the range of temperatures and pressures important for industrial applications. Our examination of reaction kinetics in supercritical water undertakes *in situ* measurements of reactants, intermediates, and products using optical spectroscopic techniques, primarily Raman spectroscopy. Our focus is to measure the primary oxidation steps that occur in the oxidation of methanol, higher alcohols, methylene chloride, aromatics, and some simple organic compounds containing nitro groups. We are placing special emphasis on identifying reaction steps that involve hydroxyl radicals, hydroperoxyl radicals, and hydrogen peroxide. The measurements are conducted in two optically accessible reactors located at Sandia's Combustion Research Facility (CRF), the supercritical flow reactor (SFR) and the supercritical constant volume reactor (SCVR), designed to operate at temperatures and pressures up to 600°C and 500 MPa. The combination of these two reactors permits reaction rate measurements ranging from 0.1 s to many hours.

The work conducted here continues the experimental approach from our previous SERDP-funded project by extending measurements on key oxidant species and expanding the variety of experimental methods, primarily spectroscopic in nature, that can be used to examine reactions at SCWO conditions. Direct support is provided to the project collaborators at MIT and Princeton who are contributing to model development for phenol, other aromatics, and halogenated species. These researchers are examining these processes using more conventional sample-and-quench methods. The experiments at Sandia and at the universities all focus on determining the primary oxidation steps that involve the OH and HO₂ radicals, generating data that will be used to evaluate and refine SCWO reaction kinetic schemes. The primary technical difficulty in this stage of the project will be recasting existing high temperature (1100 °C) chemical kinetic models for these simple molecules to 400-600 °C.

Executive Summary of Progress this Period

Programmatic

The annual SERDP in-process project review occurred May 14, 1996, at Ft. Belvoir, VA. Positive feedback from several members of the technical review committee was given verbally. Notification of the August 17, 1996, FY97 Execution Plan due date was given.

This quarter marked the arrival of Melissa Pecullan, the primary graduate student working on this project at Princeton University. She will begin a three-month visit to join the SCWO team at Sandia conducting experiments at intermediate and high pressure designed to correlate the results on the oxidation and pyrolysis of anisole and phenol that Melissa recently obtained at Princeton at atmospheric pressure to our more extreme hydrothermal conditions.

This quarter, the project has also welcomed Micheal Tucker, an undergraduate visiting for three months from Brown University. He has completed his third year in chemical engineering and has been assisting with the experimental work on the phenol/anisole reaction chemistry experiments.

The contract with Princeton University was renewed with an updated statement of work for the second year (July 1, 1996 - June 30, 1997).

H₂O₂ thermal decomposition

A great deal of data was obtained on the thermolysis rates of hydrogen peroxide at temperatures up to 440 °C and over a pressure range of 5.0 - 34.0 MPa. Several important observations can be made. First, the thermal decomposition rate of H₂O₂ at elevated pressure in the 350 - 450 °C temperature range is significantly faster than

is predicted by extrapolation of the elementary reactions in pressure and temperature from combustion conditions. There are several other interesting aspects of the data suggesting that the mechanism for the decomposition reaction in supercritical water may be significantly different than that suggested by the gas phase model.

CO/CO₂ water-gas shift chemistry

Measurements made at the end of the last quarter, clearly indicating a major change in the reaction rate of $\text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2$ at densities near the critical density, have forced us to make a major modification to the SCVR. We have added a stirring blade that has now made this reactor significantly more versatile. The old configuration was limited by the effective mixing time (controlled by diffusion and thermal gradient convection) of about 2-3 minutes. This prevented accurately following reactions with effective time constants much less than 10 minutes. The mixing feature now permits the examination of reactions that take place on the order of about 1 minute with an effective mixing time of less than ten seconds.

Massachusetts Institute of Technology, Department of Chemical Engineering

Conversion data for benzene oxidation in SCW have been obtained. The preliminary results indicate that benzene reacts minimally, if at all, under hydrolysis conditions at temperatures up to 600 °C. Therefore, benzene is a relatively refractory compound in supercritical water, which will require higher temperatures and longer residence times to obtain complete conversion. There is continued effort to compare methanol oxidation rates obtained in the MIT bench-scale, tubular reactor with those obtained from Sandia's larger tubular flow reactor.

Princeton University, Mechanical and Aerospace Engineering Department

A model for the pyrolysis of anisole, consisting of 66 reversible reactions involving 31 species, has now been developed. Excellent agreement is obtained between experimental data and predictions of methylcyclopentadiene and total phenolics, the sum of phenol and cresols. This quarter M. Pecullan arrived for a three month visit at Sandia to attempt some intermediate pressure experiments on phenol and anisole. These experiments are intended for comparison with those performed at Princeton at 1 atm and the same nominal temperature in a nitrogen bath. Since the Supercritical Fluids Reactor (SFR) was designed to operate at lower temperatures (375-650 °C) and higher pressures (25.0 -50.0 MPa) than those required for the current investigation, a substantial amount of redesign and assembly modification was necessary to achieve the desired experimental conditions.

Future work

The work next quarter will focus on completing these three experimental tasks now underway and configuring the flow reactor to handle feeds of N₂O gas dissolved in supercritical water. In addition, a paper will be prepared to be submitted to High Temperature and Materials Science on the design and application of our techniques for providing optical access to high-temperature pressurized vessels.

Detailed Summary of Technical Progress this Period

Sandia Combustion Research Facility

H₂O₂ thermal decomposition

This quarter, a significant amount of new data was obtained for the thermal decomposition of hydrogen peroxide in supercritical water and in high pressure steam. The data show that, to get a clear picture of the pressure and temperature dependence of the reaction rate, the experimental range of the residence time needs to be expanded. In addition, we completed a series of experiments examining the effect of the reactor surface on the overall conversion of H₂O₂ to oxygen and water and have found that this effect is not negligible at supercritical conditions and is probably also important in the 5-25 MPa region as well. However, we have determined that it is not the dominant process; good homogeneous rates can be determined by simply correcting for the contribution to the disappearance of H₂O₂ from the inhomogeneous pathway.

Figure 1 shows the raw data set in Arrhenius format that has been obtained to date on hydrogen peroxide thermal decomposition in water, covering the temperature range from 140 °C to 440 °C. The highest pressure data, at 34.0 MPa show a fairly smooth transition from the liquid-like densities at 300 °C ($\rho = 0.756 \text{ g/cm}^3$) to dense gas conditions at 440 °C ($\rho = 0.211 \text{ g/cm}^3$). The apparent activation energy, represented by the slope of $\ln(k)$ vs. $1/T$, increases at temperatures above the critical temperature. The lower pressure data, which have a phase transition, have an abrupt change in the rate constant at the transition from liquid to gas. Note that at 5.0 MPa there is a small temperature range where the composition is two-phase, where meaningful data cannot be obtained. More surprising however, is the observation that the rate is significantly faster at lower pressure. It appears that the higher densities present at the supercritical or liquid conditions, serve to slow the effective thermal decomposition rate.

A second important observation is that the apparent rate constant for



which is twice the unimolecular dissociation rate constant for the reaction



(see 1/96-3/96 Quarterly Report) is greater than that predicted using the best available parameters for the high-pressure-limit, gas-phase rate¹. For example, the high-pressure-limit Arrhenius expression is $k_\infty = 3 \times 10^{14} \exp(-24400/T)$. At 440 °C this yields $k(440\text{ °C}) = 0.41\text{ s}^{-1}$ compared to the observed value at 34 MPa of 4.6 s^{-1} (for Reaction 2 using the steady state approximation that $k_{\text{rxn1}} = 2k_{\text{rxn2}}$). This difference has important implications regarding the use of the gas phase value from the literature in elementary reaction models.

More data needs to be obtained to identify the higher temperature trends for 5 and 10 MPa. We hope to be able to modify the flow reactor to get data at temperatures as high as 500 °C. In addition, the unusual temperature dependence of the 5 and 10 MPa data near the phase change, showing nearly temperature-independent reactivity needs to be verified.

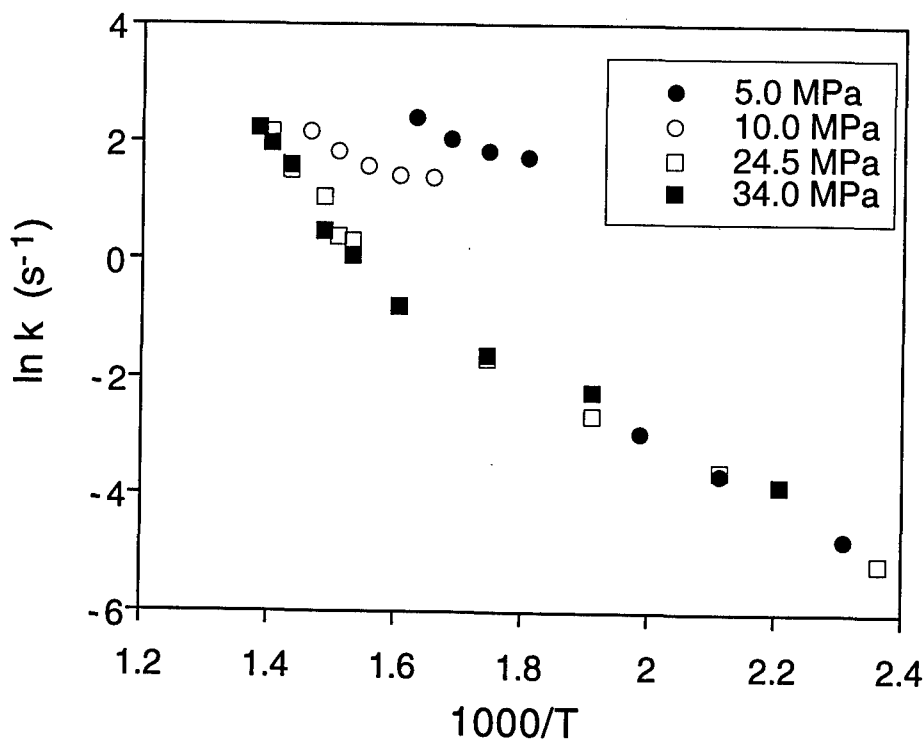


Figure 1 Plot of the observed first order rate constant for the decomposition of H_2O_2 at various temperatures and pressures. These data have not been corrected for wall effects (see below).

A concern regarding flow reactor experiments is the potential for the walls of the reactor to affect the observed rates. Since the decomposition of hydrogen peroxide is known to be catalyzed by metals, there is particular concern here that these data could be influenced by wall reactions and consequently not representative of the true homogenous thermal decomposition rate.

Figure 2 shows the results of a series of experiments examining the apparent reaction rate constant as a function of the reactor surface to volume (S/V) ratio. To carry out these measurements the 9/16 in. O.D. (3/16 inch nominal I.D.) tubing used in the SFR was filled with seven thin-walled 1/16 in O.D tubes, arranged in a hexagonal pattern such that the surface to volume is increased by almost a factor of seven. Because of experimental constraints, low conversion (high C/C_i) values have not yet been obtained. However, the data in Figure 2 show that the reaction rate appears to be faster over the first several orders of magnitude, independent of the S/V ratio; the effect appears to be more pronounced at higher rates. Clearly, there is an effect on the overall conversion rate due to the increased surface area.

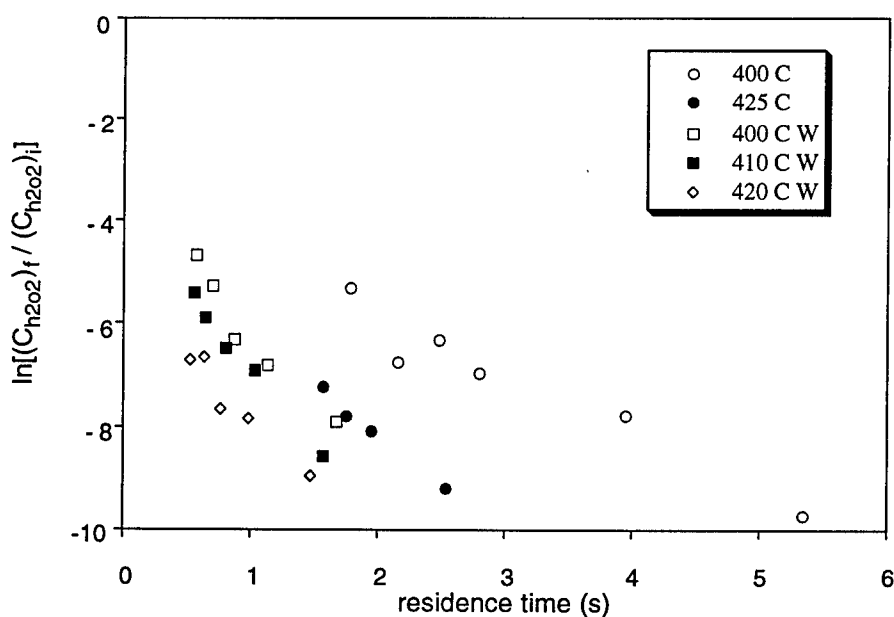


Figure 3 shows the measured experimental rate constant at the two surface-to-volume ratios. Clearly, the tube-filled reactor shows a noticeable surface effect. It also shows that extrapolation to a S/V of zero produces modestly different values for the homogeneous rate from those obtained in the normal configuration. However, these results indicate that the normal configuration experiments were conducted at sufficiently low S/V that the true homogeneous rate does not differ to an extent that a large correction is required from the observed rate and the trends in Figure 1 for the supercritical conditions will not change when corrected for this effect. However, note that we have not examined this effect at 5 and 10 MPa. There exists a concern that the lower density data may be more sensitive to the surface effects since, at lower density, a greater proportion of the collisions a reactant experiences is a wall collision, since there is less buffer gas. This will be examined next quarter.

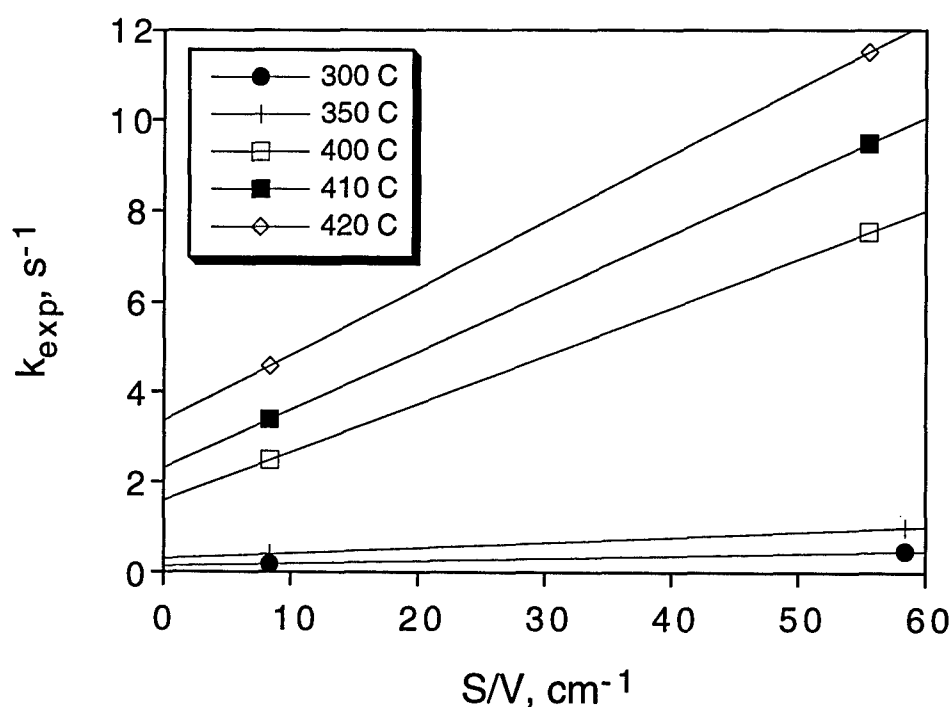


Figure 3 Plot of the observed experimental rate constant as a function of surface-to-volume ratio at several temperatures and 24.5 MPa.

CO/CO₂ water-gas shift chemistry

The result obtained last quarter showing the significant increase in the reaction rate of $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ at densities near the critical density of water at 450 °C resulted in the need to make a major modification to the SCVR. In order to examine reaction rates that are on the order of tens of seconds, the effective mixing time of the system needed to be shortened. Figure 4 shows the measured

concentration of N_2 , an unreactive surrogate for CO, monitored every ten seconds following injection in the SCVR. The time it takes for the signal to stabilize is about 200 s. Mixing in this system is controlled by convection from the injector jet (lasting about 10 s). After injection there is a longer mixing timescale that is controlled by convective eddies, due to small (approx. 1-2 °C) thermal fluctuations in the system. Thus, reactions that have effective time constants much faster than 5 times 200 seconds cannot be properly studied with this equipment.

To remedy this, this quarter we have designed and implemented a stirring system that rapidly mixes the injected reactant. Figure 5 shows a schematic of this device and Figure 6 shows how it is installed in the SCVR. The stirrer is driven by a variable speed electric motor attached to a flexible drive shaft. It is operated at approximately 100 rpm for 10 seconds. Figure 7a shows the data obtained from a typical experiment at 50 MPa (~7500 psi) and 450 °C without stirring. Note the initial overshoot in the measured amount of CO during the first two minutes of data collection, similar to the N_2 data in Figure 4. Figure 7b shows the results of an experiment at nearly identical conditions, but with the stirrer in operation. There is no overshoot in the CO concentration and the effective experimental reaction time has been reduced from about 10 minutes to near 20 seconds.

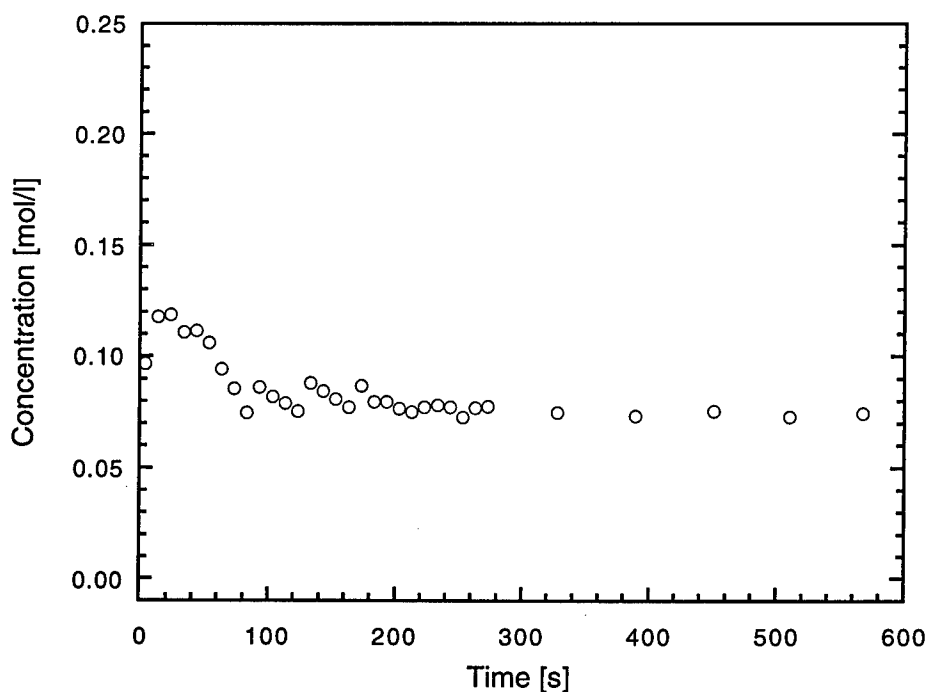


Figure 4 Plot of the observed concentration of nitrogen gas in supercritical water at 52.0 MPa and 450 °C flowing injection. The Raman signal fluctuates for the first several minutes due to fluctuation in the concentration in the probe volume.

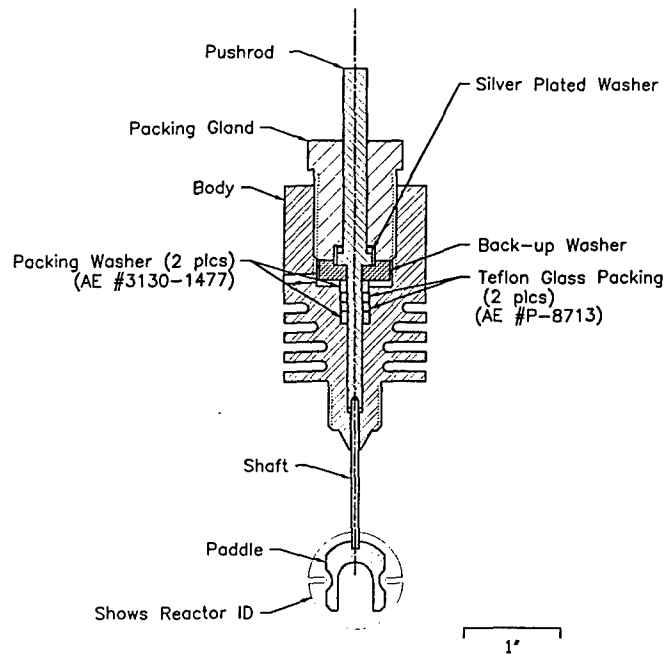


Figure 5 Schematic of the high-pressure, high-temperature feed-through stirring system.

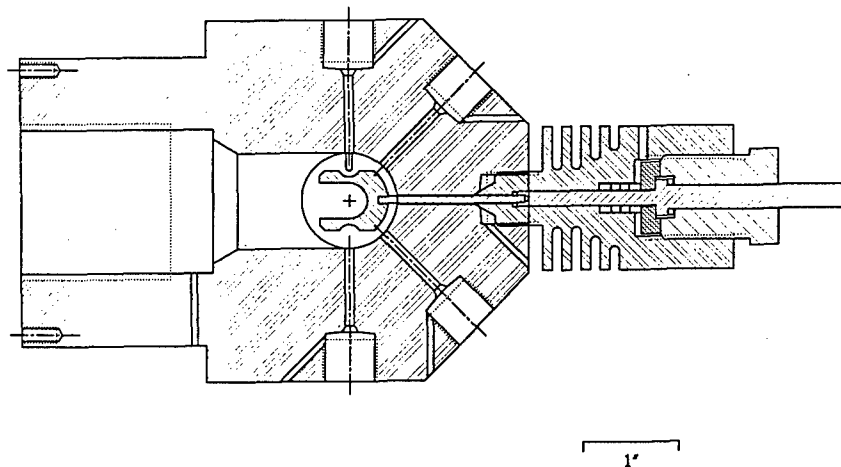


Figure 6 Schematic of the high-pressure high-temperature feed through stirring system as it is installed in SCVR. Note that the horseshoe stirring blade is designed such that when positioned properly it does not interfere with input laser beam or the scattered light collection.

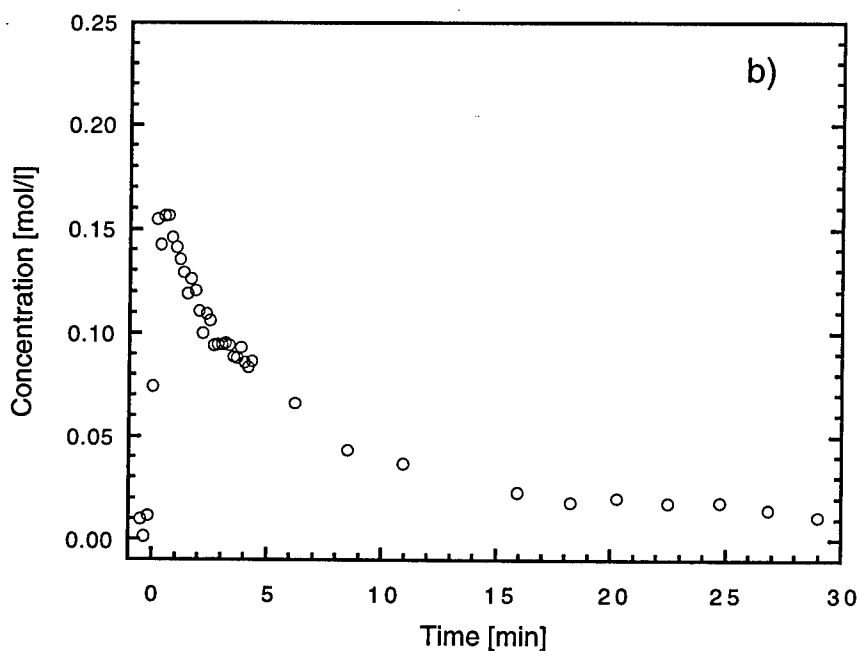
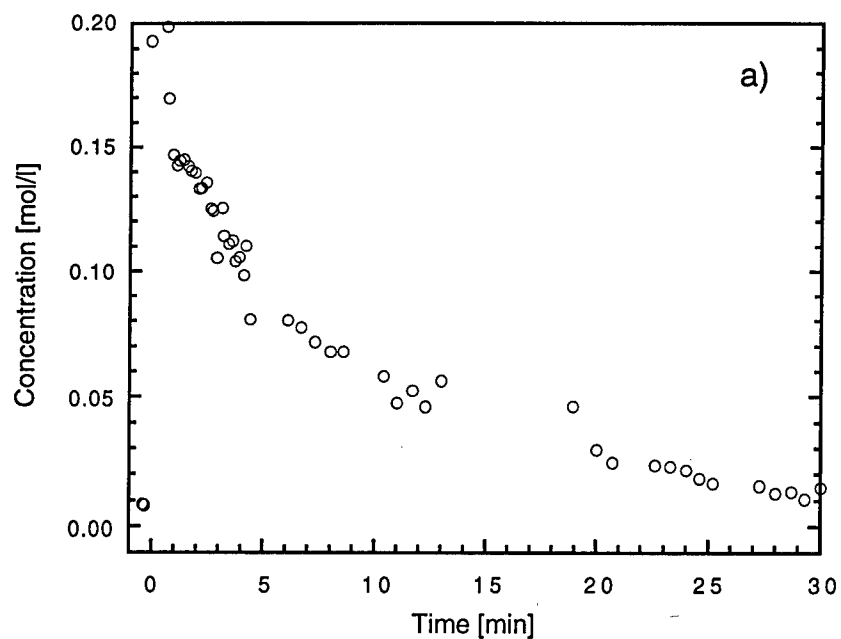


Figure 7 a) Observed concentration of CO reacting in supercritical water at 52 MPa and 450 °C without the stirrer. b) Observed concentration of CO reacting in supercritical water at identical conditions with the stirrer operated for the first 10 seconds. Note the consistent data during the first minute of reaction.

Massachusetts Institute of Technology, Department of Chemical Engineering

This work was supported partly by the Sandia (SERDP) program and partly by the Army Research Office University Research Initiative (ARO URI) program.

Comparison of SCWO methanol kinetics.

We are continuing our effort to compare methanol oxidation rates obtained in the MIT bench-scale, tubular reactor with those obtained from Sandia's larger tubular flow reactor. As highlighted in our last quarterly report, the comparison effort thus far has focused on the validation of the bench-scale hydrogen peroxide delivery system and on the redesign of the MIT reactor mixing tee to enhance mixing rates between the organic and oxidant feed streams. The mixing tee redesign effectively reduced the observed induction period to 1 second or less. With these efforts complete, recent methanol data from the two laboratories were found to be in closer agreement – though the remaining discrepancies were substantial enough to warrant further investigation.

Further examination of the equipment has raised the possibility that there may be a systematic temperature measurement error in past MIT data. The error may arise due to cooling of the oxidant and organic feed streams in the transfer lines between the preheat system and the reactor. The resulting temperature drop is not detected at the thermocouple in the inlet of the reactor due to the fact that the junction temperature is dominated by conductive heat transfer down the thermocouple sheath rather than by convective heat transfer from the fluid. Recent experimental work revealed that the oxidant and organic feed streams exiting the preheating system may have been cooled substantially in the transfer line between the preheat system and the reactor. This, coupled with the thermocouple measurement problem, may explain the remaining discrepancy between the two methanol data sets.

Efforts are currently underway to reduce the heat losses in the transfer lines and to obtain a better measurement of the true fluid temperature at the reactor inlet. After this work is completed, the joint methanol oxidation experiments will be conducted at Sandia and MIT under well-defined experimental conditions so that a direct comparison can be made between the kinetics obtained from the two systems.

Kinetics of aromatics in supercritical water

In the coming year, the main focus of research under the SERDP program will be on the SCW reaction kinetics of aromatics, with an initial concentration on benzene and phenol. Using the bench-scale, tubular flow reactor, we will measure rates and extents of benzene and phenol disappearance as affected by temperature, pressure/density, and inlet oxidant and aromatic concentrations. Experiments will

also be conducted without the addition of oxidant in order to determine the level of conversion by hydrolysis. Using these data, we will develop global kinetic rate expressions for both phenol and benzene conversion. In addition, we will identify and quantify the major reaction intermediates. For phenol, comparisons will be made with existing data from the University of Michigan and the University of Texas at Austin.

Preliminary conversion data for benzene oxidation in SCW appears in Fig. 8. The data shown were taken at 575°C and 24.6 MPa over a residence time range of 1 to 6 seconds. The initial benzene concentration was maintained at 0.5 mM at the reactor inlet. Hydrogen peroxide was used as the oxidant instead of dissolved oxygen in order to achieve the high oxygen concentrations needed, and an H_2O_2 solution was prepared to deliver a stoichiometric level of oxygen at the reactor inlet. As is apparent from Fig. 8, benzene reacts rapidly under these conditions, with conversion greater than 30% at a residence time of only 1 second. To determine the level of conversion under hydrolysis conditions, experiments were performed without the addition of oxidant. Table 1 shows that the benzene conversion obtained under hydrolysis conditions at 500, 550 and 600°C remained very near to zero, indicating that benzene reacts only minimally by hydrolysis.

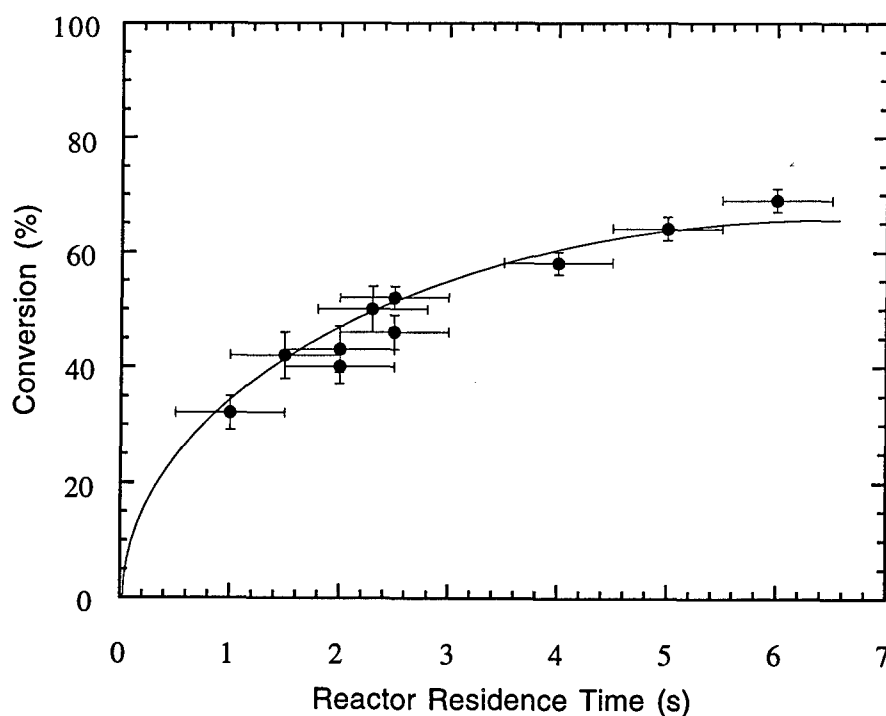


Figure 8 Conversion vs. time plot for the oxidation of benzene in supercritical water at 575 °C.

Table 1. Benzene Conversion via hydrolysis (no added oxygen)

Reactor Temperature °C	Conversion
500	-2±6%
550	3±4%
600	5±3%

GC-FID and GC-TCD were used for the identification and quantification of benzene and its partial and final oxidation products. Low molecular weight, gas-phase hydrocarbons were analyzed using GC-FID with a 30m x 0.32 mm Astec GasPro™ capillary column. Permanent gases (oxygen, nitrogen, hydrogen, carbon monoxide, and carbon dioxide) were analyzed via GC-TCD using a 5' x 1/8" OD packed Carboxen 1000 column connected via an air-actuated switching valve with a 8' x 1/8" OD Molesieve 5A column. Liquid analysis was performed using GC-FID with a 30 m x 0.53 mm Supelco SPB-1 capillary column preceded by a 2.5 m x 0.53 mm Restek Hydroguard™ column. The partial and final oxidation products that have been identified are phenol, carbon monoxide, carbon dioxide, methane, ethane, ethylene, acetylene and propylene. Carbon balances (moles of carbon recovered in products/moles of carbon in feed) range from 90-105%, leading to the conclusion that the major carbon-containing products have been identified. No effort has been made at this point to look for higher-molecular weight condensation products.

The preliminary results indicate that benzene reacts minimally, if at all, under hydrolysis conditions at temperatures up to 600 °C. Therefore, benzene is a relatively refractory compound in supercritical water which will require higher temperatures and longer residence times to obtain complete conversion. Confirming experiments will be performed on both the hydrolysis and oxidation data already obtained. Next we will determine the dependence of benzene kinetics on temperature, pressure/density and initial oxidant and aromatic concentrations. Further analytical work will be performed to identify the remaining partial oxidation products, which will include analyzing for cyclopentadiene, a major intermediate in benzene combustion. Following benzene, similar experiments will be performed using phenol.

Hydrolysis of methylene chloride in sub- and supercritical water

Our data from hydrolysis and oxidation experiments of methylene chloride (CH₂Cl₂), have been analyzed further to account for the breakdown that is occurring in the preheater tubing under subcritical conditions. The experiments were originally performed in our tubular reactor system at 246 bar and a temperature range of ambient to 600°C. Residence times varied from 7 to 17 s during heatup and 4 to 9 s at final (isothermal) temperature. CH₂Cl₂ conversions ranged from 26±9% to

99.9±0.1%. Significant conversion occurs in the nonisothermal preheater tubing section under subcritical conditions, as well as in the supercritical (> 374°C, 221 bar) isothermal section maintained at a temperature between 450-600°C. Oxygen (O₂) (added at the beginning of the isothermal section) has a significant effect on CH₂Cl₂ conversion only at temperatures above 525°C. Major products from CH₂Cl₂ hydrolysis and oxidation are formaldehyde (HCHO), hydrochloric acid (HCl), carbon monoxide (CO), carbon dioxide (CO₂), methanol (CH₃OH), and molecular hydrogen (H₂), with small amounts of methane (CH₄) observed at temperatures above 562°C. For the conditions studied, essentially all the chlorine is converted to HCl with only trace quantities of chloromethane (CH₃Cl), chloroform (CHCl₃), 1,1-dichloroethylene (C₂H₂Cl₂), cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and trichloroethylene (C₂HCl₃) detected in the gaseous product stream. Under oxidation conditions, essentially all of the carbon is converted to CO₂ by a final temperature of 600°C and a total residence time, i.e. for heatup and holding at final temperature, of 23 s.

The occurrence of CH₂Cl₂ hydrolysis during heatup at subcritical conditions was evidenced by: 1) similar reaction products, i.e. HCHO and HCl, to those identified in literature studies of CH₂Cl₂ hydrolysis under subcritical conditions; 2) corrosion in the preheater tubing attributed to CH₂Cl₂-derived HCl; and 3) similar CH₂Cl₂ conversions with and without heating in the supercritical isothermal section. CH₂Cl₂ temperature-time histories in the heatup section were determined from heat transfer calculations. We are currently trying to generate best-fit kinetic parameters for CH₂Cl₂ hydrolysis by nonlinear regression of the experimental CH₂Cl₂ conversion data against predictions of a global rate model using the calculated CH₂Cl₂ temperature-time histories in the preheater and isothermal reactor sections. Drawing on the literature, the present data, and equilibrium calculations to estimate whether certain reaction channels are thermodynamically favorable, a reaction network for CH₂Cl₂ hydrolysis and oxidation has been proposed. Major steps include reaction of CH₂Cl₂ and H₂O to form HCl and HCHO; HCHO decomposition to H₂ and CO; and CO conversion to CO₂ and more H₂ via the water gas shift reaction. In the presence of O₂, direct oxidation of HCHO and CO to CO₂ and H₂O also occurs, and becomes increasingly dominant at higher temperatures.

Princeton University, Mechanical and Aerospace Engineering Department

Kinetic modeling

As reported previously the high-temperature, gas-phase pyrolysis and oxidation of anisole have been investigated at atmospheric pressure. At the experimental conditions employed (T=1000 K, ϕ =0.62-1.71), the destruction of anisole was found to

proceed exclusively via homolysis of the $\phi\text{O-CH}_3$ bond. The reaction intermediate yields were, with few exceptions, insensitive to stoichiometry. It is inferred that, even in the presence of oxygen, the chemistry is primarily pyrolytic. Thus, accurate characterization of the pyrolysis chemistry is essential to the development of a model for the oxidation of anisole.

A model for the pyrolysis of anisole consisting of 66 reversible reactions involving 31 species has now been developed. Elementary reaction rate parameters for which measured values do not exist were obtained from thermodynamic estimations, QRRK analysis, semi-empirical molecular orbital calculations, or by comparison with analogous reactions. Model predictions of anisole decay and CO production, descriptors of overall reaction progress, match well with experiment. Excellent agreement is also obtained between experimental data and predictions of methylcyclopentadiene and total phenolics, the sum of phenol and cresols. Predictions of benzene and cyclopentadiene, minor species, are reasonable. The model's primary shortcoming is its inability to predict the production of phenol; while total phenolics are successfully modeled, the split between phenol and cresols is in error. At longer residence times, phenol constitutes approximately half the measured yield of phenolics. In contrast the model overpredicts cresols by a factor of two and, essentially, does not predict phenol. Accordingly ethane and methane are underpredicted.

The difficulty in predicting successfully the fate of the phenoxy radical in intermediate to high temperature combustion experiments is pandemic.²⁻⁶ Other investigators have suggested the conversion of phenoxy to phenol via heterogeneous chemistry, i.e. at the reactor wall.^{2,3} The possibility of wall-mediated chemistry was investigated in the context of the current anisole study. It was found that model profiles could be corrected by the inclusion of surface reactions. However, the hypothesis of surface chemistry was not supported experimentally since a doubling of reactor surface to volume ratio was found not to affect product distribution.

Experimental results

As reported last quarter, the water-perturbed pyrolysis and oxidation of anisole at 1 atm were investigated. Experiments were performed at initial water fractions of 2 and 4%. At these water loadings, the anisole chemistry was found to be unaffected. This quarter at Sandia, the pyrolysis of anisole in H_2O at 20 atm ($T=730^\circ\text{C}$) has been attempted. These experiments were intended for comparison with those performed at Princeton at 1 atm and the same nominal temperature in a nitrogen bath.

Since the Supercritical Fluids Reactor (SFR) was designed to operate at lower temperatures ($375\text{--}650^\circ\text{C}$) and higher pressures of (22-43 MPa, 3250-6300 psi) than those required for the current investigation, a substantial amount of redesign was necessary just to achieve the desired experimental conditions. The SFR's original

preheat subsystem, intended for operation in the supercritical regime, did not provide adequate heat transfer to reach the 730 °C goal temperature at the chosen pressure of 20 atm. The density of water at 730 °C and 20 atm is two orders of magnitude lower than the density of the supercritical fluid and, thus, heating is far less efficient. Therefore, the preheat subsystem itself was modified to enhance heat transfer to the gas-phase flow. Prior to modification the preheat section consisted of 3.1 meters of 14.3 mm (9/16") O.D., 4.8 mm (3/16") I.D. Inconel 625 tubing heated in stages by four 875 W radiative furnaces followed by several insulated 375 W resistive cable heaters. The sections of tubing contained within the furnaces were replaced with four coiled 8 ft lengths of 1/16" O.D. Inconel tubing. In addition, a compressed air ballast was installed just upstream of the furnaces to damp pulses of the peristaltic pump which delivers the water feed to the preheat subsystem. This precaution was motivated by concern for fatigue failure of the 1/16" tubing due to force fluctuations associated with cycling of the pump. Finally, additional cable heaters and insulation were installed downstream of the furnaces to reduce heat loss from the latter stages of the preheater.

Data collected in the current investigation were to be compared with the data set acquired at Princeton in order to gain some insight into the effect of elevated pressure and of the water bath gas. Thus, it was desired to match all other experimental conditions—temperature, residence time, and initial anisole concentration—with those employed in the Princeton study. The residence time requirement was easily met by sampling in the early part of the test section. The temperature requirement was met by implementing the changes described above. The concentration requirement, however, presented an obstacle which, ultimately, could not be overcome. The HPLC pump which delivers the fuel to the injector could not be operated reliably at the low (<0.1 ml/min) flow rates required to give the appropriate anisole concentration in the reactor. In order to run the pump within a range at which it was determined to operate reliably and still deliver the desired flow rate of anisole, a solution of anisole in water was prepared. Anisole was determined to be soluble in water only up to approximately 0.1 wt%. Now, to achieve the appropriate anisole flow rate, the required solution flow rate was too great; the temperature of the reacting flow could not be maintained at 730 °C in the vicinity of the injector.

The concentration requirement was then abandoned. A fuel flow rate was chosen at which the HPLC was shown to operate reliably. But at the increased flow rate the neat fuel was found to pyrolyze in the short, heated portion of the injector, producing solid carbonaceous material and ultimately plugging the injector. Prior to plugging, however, samples were collected. The samples were milky white to light brown in color and appeared to contain a large amount of insoluble material. GC analysis of these samples did not yield any interpretable results. Next, the heated portion of the injector was shortened and a solution of 30 wt% H₂O₂ was used to flush the injector periodically during the course of an experiment. This alleviated the problem of plugging, but did not improve the quality of the samples. It was hypothesized that most or all of the fuel was still being pyrolyzed in the injector. In

an attempt to mitigate the problem of pre-injection pyrolysis, the 0.1 wt% anisole solution was tried again. The flow rate was chosen to be sufficiently low in order to maintain the desired temperature at the injection point. However, under these conditions, the initial anisole concentration in the reacting flow was too low to obtain repeatable, reliable results from GC analysis of the samples, i.e. the GC's lower detection threshold was encountered.

While the anisole experiments have not yielded quantitative results, the reconfiguration of the SFR for higher temperature, lower pressure operation was successful and an investigation of phenol at similar conditions has commenced. Phenol is soluble in water up to approximately 8 wt%. Furthermore, the activation energy for the unimolecular decomposition of phenol is sufficiently high to preclude any fast pyrolysis in the injector.

Future Work

The work next quarter at Sandia will focus on wrapping up the three experimental tasks now underway (i.e. determination of the kinetics for the reactivity of phenol, H_2O_2 , and CO in supercritical water) and configuring the flow reactor to handle feeds of N_2O gas dissolved in supercritical water.

Three issues remain to be resolved in the H_2O_2 work. When completed, this series of experiments will provide a quantitative measurement of the thermal decomposition rate of H_2O_2 in supercritical water. Experiments are needed to:

1. = resolve the high-conversion decrease in the reaction rate and determine if this is an experimental artifact due to the small concentration of H_2O_2 being detected, or due to an unexpectedly large value for the equilibrium concentration of H_2O_2 in supercritical water/oxygen solutions.
2. collect lower conversion and shorter residence time reaction rate data for supercritical and high - temperature lower-pressure conditions.
3. determine if the 5 and 10 MPa data are significantly affected by reaction at the walls.

The equipment problems in the CO/ CO_2 experiments have been resolved by the addition of the stirring system to the SCVR and collection of a complete data set at 450 °C, 410 °C, and 480 °C can proceed. These data will permit determination of the variation in activation energy for the water gas shift reaction over a range of densities and, based on the preliminary measurements, confirm the presence of a water-assisted reaction pathway.

The difficulties with reacting anisole in the modified SFR have caused us to shift our attention to phenol. The next quarter will focus on collecting a good data set for phenol oxidation and pyrolysis at 2.0 MPa, including phenol disappearance and a gaseous product profile set. Ultimately the phenol data should be equally as useful as the anisole data in developing a model for low and high density aromatic oxidation in high pressure steam and supercritical water.

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